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(54) Manufacturing Method for High Absorbance Resin Flakes

Detailed Explanation of Invention

This invention pertains to the manufacturing method of a high absorption rate, high moisture retention, high gel-strength resin flake absorbent.

Currently, a high absorbance resin flakes have been used for sanitary products such as sanitary napkins or disposable diapers etc., as water retention material in construction and gardening; also, the flakes have been used in the coagulation of precipitates, dehydration of oil, and in architectural materials as moisture removal and shrinkage prevention.

Furthermore, the applications have been widened to include engineering plastics and toys.

Conventionally, sanitary napkins and disposable diapers were made of natural products such as fabrics or cotton and the moisture was absorbed by a physical process; thus, the absorbed water will be released upon an application of pressure, which is a disadvantage. But sanitary napkins or disposable diapers based on a water absorbing resin withstand an external pressure and have a high absorption rate because the resin absorbs moisture by a chemical process and a physical process.

The manufacturing methods include side chain reaction of starch with acrylic acid and neutralization (US Patent 4,076,663) and the use of a sodium salt of cross-linked polyacrylic acid

prepared by reverse-phase suspension polymerization (US Patent 4,093,776); but those products have a low absorption rate which is a disadvantage for use in sanitary napkins or disposable diapers.

Therefore, a number of methods for increasing the absorption rate have been carried out. An example is the sodium salt of polyacrylic acid which is obtained by reverse-phase suspension polymerization in the presence of a cross-linking agent. The water content was controlled to less than 35 weight percent and the product was further cross-linked to provide a cross-linked surface on the particles (US Patent 4,497,930). In the polymerization process, an excessive cross-linking takes place and the effectiveness of a post treatment was not significant; hence, this does not contribute to an increase in the absorption rate and, also, the gel strength is low.

Generally, the performance of a high water absorbance resin is dependent upon the absorption rate, the absorption capacity of water, and gel strength. The cross-linking ratio of the surface of a water absorbing resin affects the absorption rate, and the cross-linking ratio of the inside of the resin affects the absorption capacity and gel strength.

The absorption rate and the absorption capacity are inversely

related with the gel strength, thus, it is desired that a water absorbing resin manufacturing method should provide a water absorbing resin with improved characteristics.

The invention pertains to a manufacturing process of a water absorbing resin flakes without the above-mentioned problems; the problems of a conventional water absorbing resin, such as tackiness due to the excess water soluble polymer content and low absorption capacity, have been solved by the investigation. Prior to the post treatment, the resin was formed to flakes and the surface cross-linking was maximized; this completes the invention.

In the invention, an alkali metal acrylate of 50-100 mole percent degree of neutralization was mixed with a water soluble radical polymerization initiating agent and cross-linking agent, then, the mixture was subjected to a reverse-phase suspension polymerization and the product polymer water content was adjusted to 30-50 weight percent, and the resulting polymer was rolled to flakes and the surface was post treated with a cross-linking agent; these are the characteristics of the invention manufacturing method.

A detailed explanation is given below.

The alkali metal acrylate used in the invention can be

obtained by reacting acrylic acid with an alkali metal hydroxide, such as lithium hydroxide, sodium hydroxide, potassium hydroxide, and calcium hydroxide, and the degree of neutralization of the aqueous solution is 50-100 mole percent, preferably 65-80 mole percent. The monomer concentration in the aqueous solution is 20-70 percent, preferably 40-60 percent.

The second most important component of the water absorbing resin is a cross-linking agent which cross-links a portion of the alkali metal acrylate in order to provide the most important properties such as absorption rate, absorption capacity, and gel strength. The proper properties of a cross-linking agent are given below.

The conditions are: first, a compound having a double bond which enables the polymerization of two units; second, a compound having a double bond which polymerize one unit and having at least one functional group which reacts with an acid-containing monomer; third, a compound having at least two functional groups which reacts with an acid-containing monomer; and fourth, a multivalent metal compound which cross-links ionically. Examples of compounds having double bonds which are able to provide two unit polymerization are N,N'-methylene bisacrylamide and polyethylene glycol diacrylate. Examples of compounds having at

least one functional group which react with a double bond or one acid-containing monomer are N-methyllol acrylamide and glycidyl acrylate.

Also, examples of compounds having at least two functional groups which react with an acid-containing monomer are ethylene glycol, glyoxylic acid, and ethylene glycol diglycidyl ether. The ionic cross-linking multivalent metal compounds are the oxides and hydroxides of alkali earth metals (calcium, magnesium, zinc). They are used preferably in conjunction with N,N'-methylene bisacrylamide during the polymerization process and ethylene glycol diglycidyl ether during the post treatment cross-linking process (surface cross-linking process).

Other possible cross-linking agents which can be used in the invention are described in US Patent 4,076,663.

The invention polymerization process is a reverse-phase suspension polymerization, and the use of a solvent is imperative. Examples are n-hexane, n-heptane, cyclohexane, etc., and the preferred one is cyclohexane.

Water soluble radical polymerization initiating agents are ammonium persulfate, potassium persulfate, and hydrogen peroxide.

In the above reactions, when the water content was less than 30 weight percent, the rolling process may not provide a

desired water absorbing resin flake due to the low moisture content.

When the water content was more than 50 weight percent, the resin adheres to the rolls during the rolling process and the post treatment may not result as expected.

Also, to stabilize the reaction, a dispersant was used and, for this purpose, sorbitan monolaurate, ethyl cellulose, CMC, etc. were used.

The above-mentioned reactions will be discussed in four parts.

(1) Neutralization Process of Acrylic Acid and Alkali Metal

In the neutralization process of acrylic acid with an alkali metal, acrylic acid was added in a reactor equipped with a condenser, a dropping funnel, and stirrer. An aqueous solution of an alkali metal compound was prepared in a beaker and this solution was added to the reactor through the dropping funnel while maintaining the reactor below 30°C. In the neutralization process, a partial polymerization will take place when the reactant temperature exceeds 45°C; special care must be taken. The resulting alkali metal acrylate monomer concentration is 20-70 percent and the degree of neutralization was 50-100 mole percent.

## (2) Reverse-Phase Suspension Polymerization

A dispersant and a solvent were added to a reactor equipped with a stirrer, a reflux condenser, an addition panel, and a nitrogen injection line, and the content of the reactor was heated to 35-80°C. The alkali metal acrylate from the neutralization process and a cross-linking agent were mixed and stirred. Then a water soluble radical polymerization initiating agent was added to the mixture. The resulting mixture was added gradually in 10-60 minute span at 75-100°C and allowed to polymerize completely in 2-3 hours. At this time the excess amount of water from the neutralization process was removed by azeotropic distillation using a Dean-Stark apparatus at 80-150°C to retain 30-50 weight percent of water so as to prevent deterioration of the cross-linking process during the post treatment.

## (3) Flattening of Polymer

The excess water removed polymer from (2) process was sieved with a 20-mesh screen to separate the solvent. The resulting polymer was rolled by two rolls at 100-200°C, 10-100 rpm, with a roll gap distance of 0.01-0.5 mm to prepare polymer flakes.

## (4) Cross-Linking Post Treatment

A cross-linking post treatment is carried out on the surface

of the water absorbing resin flakes obtained from the previous process by using a cross-linking agent to increase the gel strength, absorption rate and absorption capacity. The post treatment was carried out by the following manner. To a reactor equipped with a condenser, a stirrer, and a dropping funnel, the polymer flakes and cyclohexane at 2-5 weight parts of polymer were added, then the content of the reactor was maintained at 80°C. To the reactor, 0.01-0.8 weight percent of (on the basis of the polymer flakes) of ethylene glycol diglycidyl ether was added and allowed to react for 1-3 hours. After the reaction, the solvent was separated by filtration. The reaction product was dried at 80-100°C in a vacuum drier for 2-4 hours to obtain water absorbing resin. The invention will be discussed in detail, and the performance of the invention water absorbing resin flakes were evaluated in 0.9% aqueous solution of sodium chloride for the duration of one minute, two minutes, and five minutes.

Example 1.

A 250 g of cyclohexane and 2.5 g ethyl cellulose (ethoxy content of 48%) were added in a 1-L capacity 4-neck round bottom plastic flask equipped with a stirrer, a Dean-Stark condenser, a pressure regulated addition panel, and a nitrogen injection line.

To drive out the dissolved oxygen, nitrogen was sparged into the flask and the content was heated to 67°C. A 36 g of acrylic acid and 15 g of sodium hydroxide were added to a 1-L capacity 4-neck round bottom plastic flask equipped with a stirrer, a condenser, and addition panel, and 50 g of distilled water were added gradually to the flask through the addition panel (It is an exothermic reaction and it requires cooling when an excess heat generates) to obtain 10 g of an alkali metal acrylate. To the monomer product, 0.04 g of N,N'-methylene bisacrylamide was added and dissolved. The monomer concentration in the resulting alkali metal acrylate is 45 weight percent. In a 100-mL beaker, 0.03 g of potassium persulfate was dissolved in 10 g of distilled water and the potassium persulfate was allowed to dissolve completely and then added to the above aqueous solution. Then the solution was sparged with nitrogen to remove any dissolved oxygen. The resulting solution was added dropwise into the plastic flask containing cyclohexane and dispersant via the pressure controlled addition panel in a one hour span. After the completion of the addition, the mixture was allowed to react for five hours at 70°C and then the content of water in the resulting polymer was adjusted to 30 weight percent by azeotropic distillation at above 80°C after removing 42.35 g of water. The

resulting polymer was separated from cyclohexane by filtration.

The polymer was passed through a pair of rolls at 180°C, with a roll gap distance of 0.05 mm, and rotating at 50 rpm.

At this time the surface cross-linking collapses and flattened polymer was resulted. Then the polymer was passed through a 20-mesh screen to attain an even size, and the polymer was filled in a 1-L capacity flask and 300 g of methanol were added. To the flask at 80°C, an aqueous solution consisting of 0.15 g ethylene glycol diglycidyl ether and 10 g water were added and cooled for two hours. After the reaction, the temperature of the content in the flask was allowed to equilibrate to the room temperature and cyclohexane was separated out by filtration. The resulting product was dried at 80°C for four hours under low pressure to obtain 68.68 g of water absorbing resin flakes. The absorption rate of the water absorbing resin flat particles was measured in 0.9% aqueous solution of sodium chloride after 1-minute, 3-minute, and 5-minute durations. The results are tabulated in Table 1.

#### Comparison 1

In the preparation of resin, the procedure of Example 1 was followed but without using N,N'-methylene bisacrylamide and

without the roller cross-linking process (The cross-linking agent used was ethylene glycol glycidyl ether) in post treatment. The results are tabulated in Table 1.

#### Comparison 2

In the preparation of resin, the procedure of Example 1 was followed but without using N,N'-methylene bisacrylamide and without the roller cross-linking process. The results are tabulated in Table 1.

#### Comparison 3

In the preparation of resin, the procedure of Example 1 was followed but without the roller cross-linking post treatment. The results are tabulated in Table 1.

#### Comparison 4

In the preparation of resin, the procedure of Example 1 was followed but with cross-linking post treatment without using rolls. The results are tabulated in Table 1.

#### Comparison 5

In the preparation of resin, the procedure of Example 1 was followed but with cross-linking agent treatment in the post treatment. The results are tabulated in Table 1.

Table 1

(1) 表 1

	(2) 흡수速率(g/g 폴리머)			(3) 흡수량(g/g 폴리머)	(4) 흡수성 수지내외 수용성 폴리머의 양(g)
	10	30	50		
7) 예시례 1	30	48	68	85	0.7
8) 비교례 1	10	25	35	65	5.2
8) 비교례 2	24	45	55	75	4.8
8) 비교례 3	15	35	40	68	2.1
8) 비교례 4	23	40	42	81	1.8
8) 비교례 5	8	25	35	67	1.2

Key to table.

1: Table 1,        2: Absorption rate (g/g polymer),  
 3: minute(s),      4: Amount of water absorbed,    5: (g/g polymer),  
 6: Content of water soluble polymer in water absorbing resin,  
 7: Example,        8: Comparison.

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\* The comparison of absorption rate, absorption capacity, and the content of water soluble polymer in 0.9% aqueous solution of sodium chloride.

Table 1 shows the characteristics of the invention high

absorption resin flakes.

The Comparison 2 specimen was obtained by self-cross-linking of Comparison 1 and, thus, the surface cross-linking was insufficient but the post treatment improved the absorption rate and absorption capacity; however, the water absorbing resin contained 2-5% of water soluble polymer which was removed from the resin, therefore, the absorption rate was high but the absorption capacity was low. This is not suitable for application.

The Comparison 4 specimen was obtained by some cross-linking and post treatment of Comparison 3 specimen. The absorption capacity did increase but the absorption rate did not. The post treatment effect was insignificant.

But the Example 1 specimen was obtained by flattening of the Comparison 5 specimen and the surface cross-linking had been collapsed with some residual internal cross-linking. A post treatment resulted in a compressed and large surface. This provided a high surface cross-linking; the absorption rate had been increased and water soluble polymer was almost none, thus, the specimen had a high absorption capacity and had no tackiness. The specimen was suited for application and the degree of cross-linking was high which increased the gel strength.

(57) Claims of Patent

1. The manufacturing method of a high absorption capacity resin is characterized that an alkali metal acrylate of 50-100 mole percent degree of neutralization is mixed with a water soluble radical polymerization initiating agent and a cross-linking agent, and the resulting mixture is subjected to reverse-phase suspension polymerization, subsequently the water content of the polymer is adjusted to 30-50 weight percent and flattened by rolls and then the surface is treated with a cross-linking agent to obtain water absorbing resin flakes.
2. In Claim 1, the manufacturing method of high absorption capacity resin flakes is characterized that the temperature of the rolls is maintained at 100-200°C in the manufacturing of the resin flakes.
3. In Claim 1, the manufacturing method of high absorption capacity resin flakes is characterized that the gap of the rolls is maintained at 0.01-0.5 mm in the manufacturing of resin flakes.
4. In Claim 1, the manufacturing method of high absorption capacity resin flakes is characterized that the rotation rate of the rolls is maintained at 10-100 rpm in the manufacturing of

resin flakes.

5. In Claim 1, the manufacturing method of high absorption capacity resin flakes is characterized that the alkali metal acrylate monomer concentration is maintained at 20-70% in the manufacturing of resin flakes.

6. In Claim 1, the manufacturing method of high absorption capacity resin flakes is characterized that the reverse-phase polymerization temperature is maintained at 35-80°C in the manufacturing of resin flakes.

7. In Claim 1, the manufacturing method of high absorption capacity resin flakes is characterized that ethylene glycol diglycidyl ether is used as the cross-linking agent in the post treatment in the manufacturing of resin flakes.

8. In Claim 1, the manufacturing method of high absorption capacity resin flakes is characterized that the amount of the cross-linking agent is 0.01-0.8 weight percent on the basis of polymer produced in the manufacturing of resin flakes.

9. In Claim 1, the manufacturing method of high absorption capacity resin flakes is characterized that the alkali metal salts are lithium hydroxide, sodium hydroxide, potassium hydroxide, and calcium hydroxide in the manufacturing of resin flakes.

10. In Claim 1, the manufacturing method of high absorption capacity resin flakes is characterized that the water soluble radical polymerization initiating agents are ammonium persulfate, potassium persulfate, and hydrogen peroxide in the manufacturing of resin flakes.

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## **Wenz I, Tina (CJ)**

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**Fr m:** Crosby, Nancy (NA)  
**S nt:** Tuesday, July 31, 2001 3:42 PM  
**To:** Wenzel, Tina (CJ)  
**Cc:** Woodbury, Richard (RP)  
**Subj ct:** FW: Confidentiality agreement covering new project

[REDACTED]  
MBA-confidentiali  
Dow.doc... Tina,

This is technology related; therefore, I'll turn this one over to you.

Nancy

-----Original Message-----

From: Woodbury, Richard (RP)  
Sent: Tuesday, July 31, 2001 10:27 AM  
To: Crosby, Nancy (NA)  
Subject: FW: Confidentiality agreement covering new project

Nancy,

Could you please take a look at this CDA. Warren Treptow or Sheldon will be signing it if it is OK. Thanks!

-----Original Message-----

From: Clarke, Russell (R)  
Sent: Tuesday, July 31, 2001 7:43 AM  
To: Woodbury, Richard (RP)  
Subject: FW: Confidentiality agreement covering new project

Rich,

As you have seen from the e-mail which I sent out, I have sent the proposed secrecy agreement from DSM to Iona, my legal contact in London.

I know that I asked you to take care of it yesterday, but if she can give me approval before I go vacation then hopefully we can get things moving.

Let me know if there is anything in the agreement which you would like to comment upon or change?

Regards

Russell Clarke  
Commercial Development Manager  
Dow Custom and Fine Chemicals  
Telephone/Fax number : (0044) 07003902775  
e-mail : rclarke@dow.com

-----Original Message-----

From: Poechlauer, Peter [mailto:Peter.Poechlauer@DSM-GROUP.COM]  
Sent: 30 July 2001 15:19  
To: 'Clarke Russel'  
Subject: Confidentiality agreement covering new project

<<SiHMBA-confidentiality-Dow.doc>>

Dear Russell,  
attached please find a standard confidentiality agreement (very much like  
the agreement covering the RCMA work).  
We ask you to sign it to enable us sending you further information on our  
new project.

Looking forward to a further collaboration,

best regards

Peter Poechlauer

Wolfgang Skranc

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